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POLYMORPHIC CHANGES UNDER PRESSURE OF THE UNIVALENT NITRATES.

By P. W. Bridgman.

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Introduction.

In this paper the thermodynamic elements involved in the polymorphic changes of a group of closely related univalent nitrates are given over a considerable pressure and temperature range. The apparatus, the experimental methods, and the methods of computation are in every way the same as were described in a previous paper [1] on a similar subject.

Particular interest attaches to the group of the univalent nitrates because of the wide occurrence of polymorphism in this group, the unusual number of polymorphic forms, and their complicated relationships. Here, one would expect, is a particularly favorable field in which to look for new forms, stable only at high pressures, which will supply the gaps at atmospheric pressure. It turns out, however, that there are comparatively few new forms in the range reached here: one new form for ammonium nitrate and two for potassium nitrate.

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[1] P. W. Bridgman, Proc. Amer. Acad. **51**, 53–124 (1915).

The data are presented in the order of complication of the phase diagrams, and include the coördinates of the transition curves, the change of volume, latent heat and internal energy, and in those cases where the measurements were sufficiently accurate, an estimate of the difference of compressibility, thermal expansion, and specific heat of the different modifications. In the discussion of the relations of the various forms it will appear that the three simplest nitrates, those of Rubidium, Caesium, and Thallium, are much alike in their behavior under pressure; the nitrates of Ammonium and Potassium are much less simple in their relations, and Silver Nitrate is apparently not connected with these at all.

Detailed Data.

Silver Nitrate.— Two batches of this substance were used. The first was from Eimer and Amend, c. p., and was used both for the run at atmospheric pressure and for the runs over the entire high pressure range. For the determinations at high pressures it was hammered dry into an open steel shell. The high pressure points were found in the order of decreasing pressure and increasing temperature. For the measurement at low pressure, the $AgNO_3$ was fused into a glass tube, in which it remained. The second batch was from the J. T. Baker Chemical Co., "analyzed chemicals," and showed by analysis less than 0.002% of impurity. This was fused into glass moulds, from which it was removed for the measurements. The moulds were of such a size that the sticks of $AgNO_3$ fitted loosely the inside of the pressure cylinder. In all cases, pressure was transmitted directly to the $AgNO_3$ by kerosene. With this second batch, five of the high pressure points were repeated, between 6000 and 12000 kgm., six months after the original determinations. Every part of the apparatus was different from the original, which had been destroyed piece by piece in the meantime by various explosions. The agreement of the p-t values of these two determinations is good. This repetition was made necessary because of an accidental distribution of error in the two lowest Δv points of the original measurements, such that there appeared to be a discontinuity in the Δv curve, so that there was consequently a possibility that another modification might exist.

No perceptible decomposition of the $AgNO_3$ could be detected where it came in contact with the steel, although such might be expected, because iron is known to deposit silver from solution. There was, however, some slight amount of decomposition somewhere, as shown by the escape of a few bubbles of gas when the apparatus was opened after the measurements at high temperatures. This decomposition might be either in the kerosene or the $AgNO_3$. No such decomposition could be detected, however, after the measurements at the lower temperatures and higher pressures. Possibly this slight decomposition might explain the two discordant points which were discarded, although there are other possibilities, such as the fact that the change of volume is so small that a very slight amount of hysteresis would produce a comparatively large error. On repeating the measurements the possibility of hysteresis was avoided as far as possible by running the pressure back and forth several times over the transition before beginning the measurements. The quantity of $AgNO_3$ used in these runs varied from 61 to 103 gm.

The direct experimental points are shown in Figure 1, the computed values of ΔH and ΔE in Figure 2, and the numerical results are collected in Table I. The only points of either determination which have been discarded are the two bad Δv points already mentioned; one of these was about 30% and the other 12% too high. In view of

TABLE I.

SILVER NITRATE.

Pressure	Temperature	ΔV cm.^{3}/gm.	$\frac{d\tau}{dp}$	Latent Heat kgm.m./gm.	Change of Energy kgm.m./gm.
1	159°.4	.00250	−.0075	1.442	1.442
1000	151 .8	254	77	1.402	1.427
2000	143 .9	259	80	1.350	1.402
3000	135 .8	265	83	1.305	1.385
4000	127 .4	272	86	1.267	1.376
5000	118 .7	279	89	1.228	1.368
6000	109 .7	287	96	1.145	1.317
7000	99 .0	296	125	.881	1.088
8000	83 .2	307	200	.548	.794
9000	56 .8	320	415	.254	.542
9500	28 .3	326	990(?)	(?)	(?)
9770	0 .0	330	——	(?)	(?)

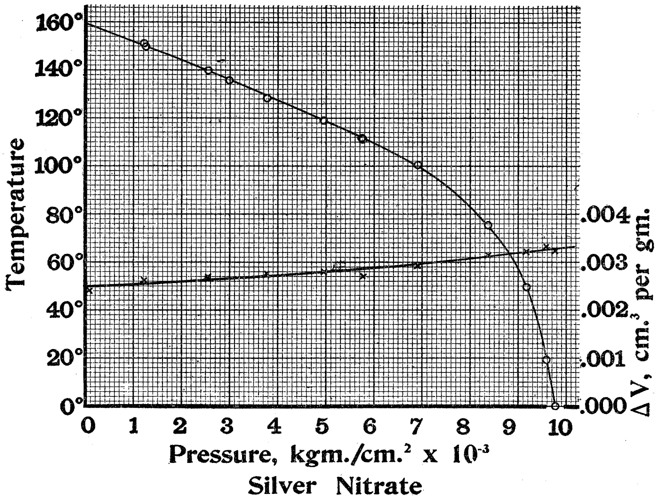

FIGURE 1. Silver Nitrate. The observed equilibrium pressures and temperatures (circles) and the observed changes of volume (crosses).

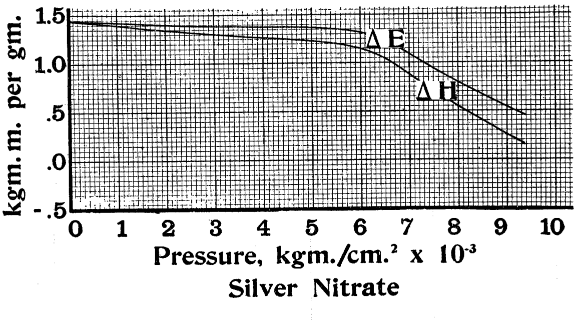

FIGURE 2. Silver Nitrate. The computed heat of transition and the difference of internal energy between the two phases.

the large probable error because of the great width of the region of indifference at the lower end of the curve, no values of ΔH or $\frac{d\tau}{dp}$ are tabulated for this part of the curve.

The feature of particular interest for $AgNO_3$ is the remarkably sudden increase of curvature of the transition line beyond 6000 kgm., a feature unique to this substance. In fact, the increase of curvature is so great that when I first found the transition at 20°, it seemed as if there must be a third modification, and that the phase diagram would look like that of AgI. The whole of the field was very carefully explored for other modifications; the strongest motive for repeating the measurements was that the discordant Δv points lent color to the suspicion that there might have been an undetected third modification near the bend with a small Δv. No other form could be found, however, to 12000 kgm. at room temperature, or at 200°, and on the repetition of the experiment none could be found in the neighborhood of the bend.

It is possible to pass over the curve at any point without the reaction starting. The width of the region of indifference within which the reaction does not run after it has once started changes in a curious way with the pressure. The detailed data for this effect are to be given in the succeeding paper.

There are several measurements of the transition data at atmospheric pressure. Schwarz[2] gives 159.2° to 159.7° by an optical method for the transition temperature, Hissink[3] finds 159.8° with a dilatometer, and Guinchant[4] gives 159°. The value found by extrapolation of the above data of my own was 159.4°. The change of linear dimensions during the transition has been measured by Guinchant,[4] who found an increase of from 0.22 to 0.25% on cooling, and a decrease of 0.17% on heating. Assuming 4.3 for the density, this is equivalent to about 0.00047 cm^3 per gm., against 0.00250 found above by direct methods. This shows that the change of volume during the transition does not take place equally in all directions, an effect shown by other substances also. Guinchant[5] has also found the latent heat of the transition to be 4.9 cal. against 3.4 found above. The agreement should be closer.

The difference of compressibility of the two modifications was directly measured at several points. These values, which are somewhat more self consistent than usual, are shown in Figure 3. At low pressures (high temperatures), the form with the larger volume is more compressible, but as we go along the transition curve to higher pressures and lower temperatures, the difference of compressibility become less, and finally reverses sign in the neighborhood of the region of rapid curvature. Below 70° the modification stable at the higher temperature is the more compressible. This is perhaps what one might be at first inclined to call the normal behavior, but it is to be noticed that there are two opposite factors here. It is natural to think that the phase of greater volume, as well as the high temperature phase would be the more compressible. Evidently both of these things cannot happen at the same time on this curve. At low pressures it is the phase of greater volume which is the more compressible, but at high pressures it is the high temperature phase which is the more compressible. The relations in this regard at the high pressure end of the curve are similar to those on the melting curve of water and ice I, where water, although of smaller volume, is more compressible than ice. It should be remarked that this reversal in the sign of the compressibility is not to be regarded as remarkable in view of the sudden change of direction of the transition curve. The transition curve is unusual in this respect; one may expect unusual features in the behavior of the two phases to correspond.

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[2] W. Schwarz, Diss. Gött. 1892; Beibl. **17**, 629 (1893).

[3] D. J. Hissink, ZS. phys. Chem. **32**, 537–563 (1900).

[4] J. Guinchant, C. R. **149**, 569–571 (1909).

[5] J. Guinchant, C. R. **145**, 320–322 (1907).

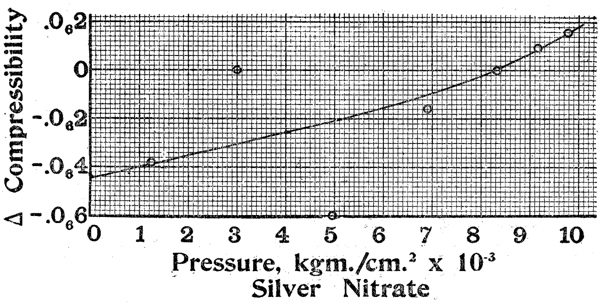

FIGURE 3. Silver Nitrate. The observed differences of compressibility between the two phases.

The differences of the expansion and of the specific heats may be calculated from the difference of compressibility, and are shown in Table II. The difference of expansion runs roughly parallel to the

TABLE II.

SILVER NITRATE.

Pressure kgm./cm.^{2}	$\Delta\alpha$	$\Delta\beta$	ΔCp kgm.cm./gm.
1	$-0.0_{6}45$	$-0.0_{4}55$	0.35
2000	$-\ .0_{6}35$	$-\ .0_{4}37$	0.21
4000	$-\ .0_{6}25$	$-\ .0_{4}22$	0.11
6000	$-\ .0_{6}15$	$-\ .0_{5}6$	0.13
8000	$-\ .0_{7}2$	$+\ .0_{5}5$	0.13
9000	$+\ .0_{7}7$	$+\ .0_{5}5$	0.08

difference of compressibility. On the low pressure end of the curve the high temperature phase is the less expansible, but at the other end of the curve it becomes more expansible. The change in sign of $\Delta\beta$ occurs at a lower pressure than that of $\Delta\alpha$. Just what the structural change in the crystal is which brings about these changes in sign of $\Delta\alpha$ and $\Delta\beta$ is difficult to say; it may be a compacting together under pressure of the crystal framework of the low temperature form which makes it less responsive to changes of temperature and pressure. The compressibility of $AgNO_3$ (II) would be expected to show considerable variations with pressure just as ice I does.

The difference of specific heat at atmospheric pressure, calculated with the above values of $\Delta\alpha$ and $\Delta\beta$, is 0.0082 cal. per gm., which agrees almost exactly with the directly determined value, 0.008, of Guinchant.[5] The difference of specific heat decreases at the higher pressures. There is no change of sign, however, but the high temperature phase has throughout the greater specific heat.

CAESIUM NITRATE. This substance was most kindly loaned by Professor Baxter, by whom it had been purified for his atomic weight work. Immediately before using it was dried in vacuum at 100° for several hours. This is a rare substance, and I was very fortunate to be able to get enough of it to work with; I take this opportunity of expressing my gratitude for Professor Baxter's kindness.

Only one sample of the substance was used, 75 gm. in amount, and both the high and low pressure determinations were made with it. It was hammered dry into an open steel shell, and pressure was transmitted directly to it by kerosene. Two determinations were made at low pressures; one by varying temperature at constant pressure to give Δv, and one by varying pressure at constant temperature to give the transition point. Four points at higher pressures, all by the isothermal method, were sufficient.

The domain of indifference is nowhere wide, but it varies greatly at different temperatures, a rather unusual effect. At 100 kgm. it was possible to shut the equilibrium pressure within limits only 11 kgm. apart; at 177° the limits were 8 kgm., at 164° 17 kgm., and 189° 70 kgm., and at 202°, 125 kgm. It is unusual that the limits at 177° were narrower than at 164°, but it is to be noticed that the 177° point was determined first; possibly the transition may have developed fissures in the solid which would account for the wider limits at 164°. It might be thought natural that along with the narrowness of the band of indifference at the lower temperatures would go a high rate of reaction, but this was not so. The reaction velocity was distinctly slower than for most solids; at 100 kgm. about 90 minutes were

TABLE III.

Caesium Nitrate.

Pressure	Temperature	ΔV cm.^{3}/gm.	$\frac{d\tau}{dp}$	Latent Heat kgm.m./gm.	Change of Energy kgm.m./gm.
1	153°.7	.00405	.0095	1.820	1.820
1000	163 .1	387	93	1.815	1.776
2000	172 .3	369	91	1.806	1.732
3000	181 .3	352	89	1.797	1.691
4000	190 .1	334	87	1.778	1.644
5000	198 .7	316	85	1.754	1.596
6000	207 .1	298	83	1.724	1.545

required to reach approximately stationary conditions, and at each of the high pressure points about 50 minutes. As for most solids, the velocity was distinctly greater with falling pressure than with rising. It is possible to pass across the equilibrium curve in either direction without the reaction starting, but only to a slight extent.

The experimental results are shown in Figure 4, the computed values of ΔH and ΔE in Figure 5, and the numerical values in Table III. The curvature of the *p–t* curve is normal; the ΔV curve falls with rising pressure, as is normal, but the experimental accuracy was not great enough to surely determine the direction of curvature, so it is drawn as a straight line.

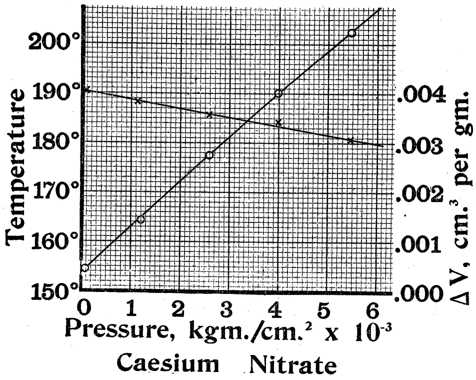

FIGURE 4. Caesium Nitrate. The observed equilibrium pressures and temperatures (circles) and the observed changes of volume (crosses).

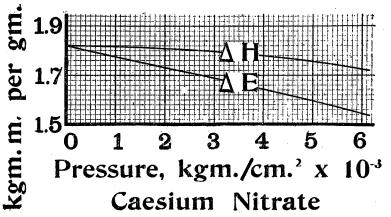

FIGURE 5. Caesium Nitrate. The computed heat of transition and the difference of internal energy.

There seems to be only one value for comparison at atmospheric pressure, 145° for the transition temperature by Wallerant.[6] The value found above for the transition temperature was 153.7°. In view of the exceptional purity of the sample used above, it would seem that 153.7° should be given the preference.

Direct measurements were made of the difference of thermal expansion of the two phases at low pressures (77 kgm.), and of the difference of compressibility at higher pressures. The measurements are better than usual, and give more consistent results. Three measurements of the difference of compressibility at high pressures were made; one of these was somewhat too large, but the other two agreed within 5%. The values follow.

At 77 kgm.

$$\begin{aligned} \Delta\alpha &= 0.0_649 \\ \Delta\beta &= 0.0_433 \\ \Delta C_p &= 1.0 \end{aligned}$$

At 5000 kgm.

$$\begin{aligned} \Delta\alpha &= 0.0_631 \\ \Delta\beta &= 0.0_415 \\ \Delta C_p &= 0.28 \end{aligned}$$

At 77 kgm., $\Delta\beta$ was the observed value, and at 5000, $\Delta\alpha$. We see that at both pressures the high temperature phase is the more compressible, has the greater expansion, and the greater specific heat. The differences between the two phases become less at higher pressures. The decrease of $\Delta\alpha$ with rising pressure was unmistakably shown by the direct measurements. This behavior of $CsNO_3$ is what one would perhaps be inclined to call entirely normal. The difference of compressibility between the two phases is of the order of the compressibility of platinum.

Especially careful search was made for other modifications, since others were expected in analogy with the other nitrates. None were found to 12000 kgm. however, at 20°, 177°, or 200°.

RUBIDIUM NITRATE. I have to thank the kindness of Professor T. W. Richards for this rare substance. He personally prepared the samples by repeated crystallization. The purification was continued until the flame test, very sensitive in these cases, showed no trace of any of the other alkali metals. The salt as finally provided by Professor Richards was crystallized from acid solution, and gave an acid reaction. It was unfortunate that I did not succeed in removing all of the acid; even heating to over 200° in vacuum for several hours was not effective. The presence of free acid was shown by the corrosion of the steel shell and cylinder after the runs were finished. Certain very puzzling inconsistencies in the behavior under pressure are probably to be explained by the presence of acid. Professor Richards has therefore undertaken to prepare a second sample, this time crystallized from neutral solution. In the preparation of this sample several unexpected delays have arisen and the way does not yet seem clear to a successful outcome. I have therefore thought it best to publish tentatively the results already obtained, and to reserve for a future note the data on the perfectly pure sample. None of the conclusions reached in this paper can be altered by a slight change in the numerical values. My unwillingness to delay longer is because the rest of the data of this paper have now been awaiting publication for somewhat over a year, and a succeeding longer paper is entirely finished, waiting only for the appearance of this paper.

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[6] F. Wallerant, Bull. soc. fr. min. (1905) 311–374.

Runs were made at three different times. The first gave five points from 1000 to 6000 kgm. These results were fairly regular; the Δv point at the lowest pressure was lower than was to be expected, however. After two months the points at approximately atmospheric pressure were determined. The equilibrium temperature was nearly 1° low, judged by extrapolation from the previous high pressure points, and Δv was 10% low. There was no possibility of accidental experimental error; two independent determinations at 78 kgm. gave very concordant results. Again after two months, four more points were redetermined at high pressures. The Δv points of this run were very much lower than the previous points and more irregular; the greatest discrepancy being 30% at 4000 kgm. The equilibrium temperatures also did not agree, at 1000 kgm. being 0.4° low, and at 4000 kgm. 1.5° high. The transition line as redetermined would, therefore, extrapolate to a lower transition temperature at atmospheric pressure. It seems probable that there was some slow permanent change taking place in the $RbNO_3$ due to the free acid. In the Figure and the Table, I have therefore given only the results of the first run, which seem more likely to be accurate.

The equilibrium pressures and temperatures and the changes of volume are shown in Figure 6, and the numerical values are collected in Table IV. In view of the certainty of revision of these data, it did not seem worth while to give a diagram as usual for ΔH and ΔE.

$RbNO_3$ is known to have another transition point at atmospheric pressure,[6] near 219°, so that there is another modification not shown on the diagram. It is for this reason that the two phases shown above are numbered II and III. I made careful search for the transition from I to II at 239° between 500 and 7000 kgm., but without success. It is very unlikely that the slope of this transition line is so

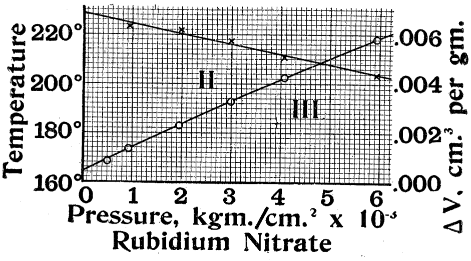

FIGURE 6. Rubidium Nitrate. The observed equilibrium pressures and temperatures (circles) and the observed changes of volume (crosses). It is to be remembered that these values are subject to revision.

TABLE IV.

RUBIDIUM NITRATE.*

Pressure	Temperature	Δv cm.³/gm.	$\frac{d\tau}{dp}$	Latent Heat kgm.m./gm.	Change of Energy kgm.m./gm.
		II–III			
1	164°.4	.00688	.00990	3.04	3.04
1000	174 .1	646	955	3.03	2.96
2000	183 .5	603	924	2.98	2.86
3000	192 .6	561	898	2.91	2.74
4000	201 .4	518	875	2.80	2.60
5000	210 .1	476	857	2.68	2.45
6000	218 .6	434	843	2.53	2.27

* These values are subject to revision.

great that at 239° the transition pressure is below 500 kgm. Failure to find the transition means either that the transition point of the pure substance is appreciably higher than 219°, or else that II will support considerable superheating with respect to I. A special run ruled out the possibility that the transition from II to I is of the ice type and had been overlooked for that reason. I also made search for new modifications at room temperature to 12300 kgm. without success.

During the first run I made measurements of the time rate of transition and of the breadth of the band of indifference. The breadth of the band varied from 100 to 200 kgm. The transition velocity is unique in that the velocity with falling pressure is less than with rising pressure. This may be an effect of the free HNO_3.

The transition temperature II to III is given as 161° by Wallerant[6] and 161°.4 by Gossner.[7] Both of these values are lower than the value found above, 164.4°. It is significant that when I repeated the run, after the substance had become impure, I found a lower value than 164.4°, about 163°. It is therefore plausible to suppose that the lower values of Wallerant and Gossner may have been due to impurity. No previous measurements of the change of volume or of the heat of transition have been made.

THALLIUM NITRATE. This salt was prepared by dissolving metallic Thallium in warmed dilute nitric acid, and by repeatedly crystallizing from aqueous solution. Preparation from the element was necessary because the nitrate is not kept in stock by any of the chemical supply houses. After each crystallization the crystals were washed; the end product was entirely free from acid reaction. The purification of this substance is particularly easy because of the great difference of solubility in hot and cold water; water at 100° dissolves about 100 times as much water at 0°. Only enough of the salt could be made for one filling of the apparatus. I used for this all the metallic Thallium available at the time in this country, and none was to be procured from abroad. The salt was hammered cold into an open perforated steel shell, and pressure transmitted directly to it by kerosene.

With this single specimen a large number of readings were made. Measurements of this substance are of unusual difficulty because of the very small changes of volume and the large amount of superpressure required to force the reaction to run. At least one unsuccessful attempt was made before even the existence of the line II–III was established. Because of the unusual difficulties, a special procedure was necessary in getting the points of the II–III curve. After the reaction had started to run, and had been perhaps half completed, pressure was artificially changed in the direction of the suspected equilibrium, and after this change the direction of secondary pressure change noted. After each change of pressure it is necessary to wait only long enough to be sure of the direction of spontaneous pressure change before making another trial. It is thus possible to obtain results very much more quickly than by waiting for pressure to be brought back to the equilibrium value by the progress of the reaction, and in those cases in which Δv is small, it is possible to shut the equilibrium pressure within much narrower limits. With the galvanometer and the bridge used the sensitiveness was great enough so that a change of $\frac{1}{4}$ kgm. could be certainly detected. This made it possible to shut the equilibrium pressure within values differing by about 50 kgm. on the I–II curve, and about 100 kgm. on the II–III curve. One must be careful, when working with such small pressure changes, not to be deceived by the effects of heat of compression, which under proper conditions simulate the appearance of a reaction.

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[7] B. Gossner, ZS. Kryst. **38**, 110–168 (1903).

The values of equilibrium pressure and temperature, shown in Figure 7 are fairly consistent. The values of ΔV, on the other hand, which are shown in Figure 8, were never satisfactory, although I used every wile at my command to get good values. The difficulty, which would be great enough in any event because of the small values of Δv, is increased by the great sluggishness of the reaction between the two phases in each other's presence, as well as by the large superpressure required to start the reaction. If one tries to complete the reaction by running the pressure far beyond the transition point, error from hysteresis is introduced. Part of the difficulty is doubtless connected with the chemical instability of the salt itself. After the series of runs, some of the salt in the lower part of the cylinder was found changed to a brick red color. Thallium, of course, forms two series of salts, univalent and trivalent, and the trivalent form of some salts is the more stable. If there were a change from a thallous to a thallic salt, the reacting volume of the thallous salt would be less, and the change of volume less. If this change did take place, it must have been toward the end of the experiment, and would suggest a reason for the low points found for Δv on the II–III curve at 11200 and 11700 kgm., and on the I–II curve at 7000 kgm. These points were measured with particular care, and there seems no doubt that they give accurately the change of volume of whatever was in the apparatus at the time. The point at 11200 was measured in the regular way by decreasing pressure at constant temperature; the point at 11700 was obtained by changing temperature at constant volume, and is the mean of two points, practically the same, obtained with increasing and decreasing temperature. For this run, the temperature was lowered to 110°, corresponding to a superpressure of 6000 kgm., to be

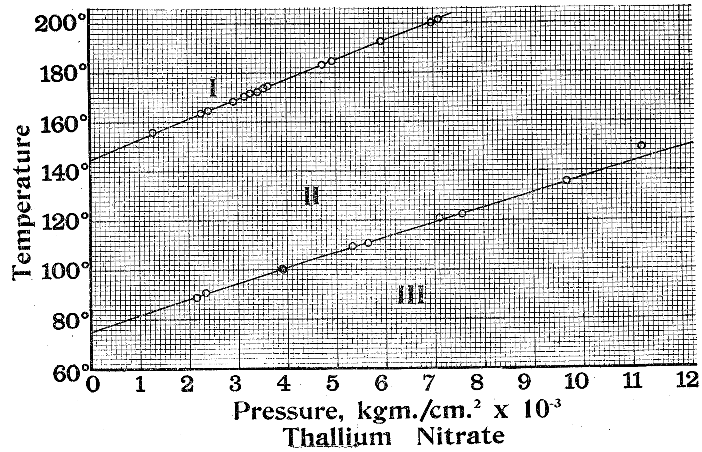

FIGURE 7. Thallium Nitrate. The observed equilibrium pressures and temperatures.

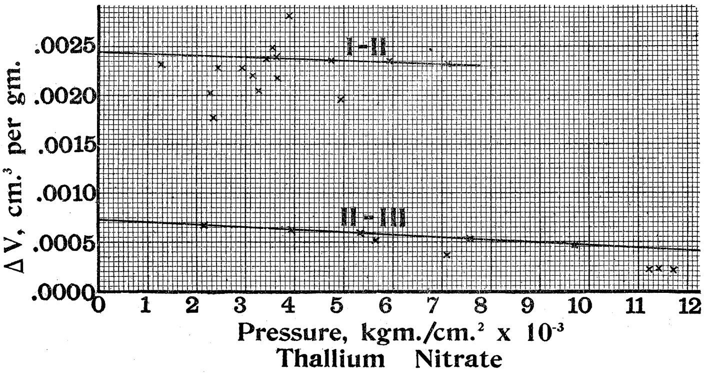

FIGURE 8. Thallium Nitrate. The observed changes of volume.

sure of completion of the reaction. The point at 7000 on the I–II curve is really three coincident points, two with falling pressure, and one with rising pressure, at constant temperature. The pressure limits for this point were twice as wide as usual, to ensure completion of the reaction.

There seems considerable reason to suspect that the high point on the upper end of the line for II–III belongs to another equilibrium line, and that there is a fourth modification. The consistently low points for the corresponding Δv bear this out. These points, when compared with the low point on the upper end of the Δv curve for I–II, are too low in proportion to be entirely explained by a partial transition to a thallic salt. This surmise was not verified; results would have been difficult of interpretation because of the known partial change of the thallous nitrate. It was also of no use to try for the usual data with the low pressure apparatus; the low pressure points are always made after the runs at high pressures, and in this case it was known that the high pressure had at least initiated some sort of a permanent change. It may be mentioned that whatever the transition product, it does not form mixed crystals with $TlNO_3$, for the p–t values were unaffected by the discordant Δv values, and the transition remained sharp throughout. Under the conditions, the best that I could do with the data was to draw a straight line through

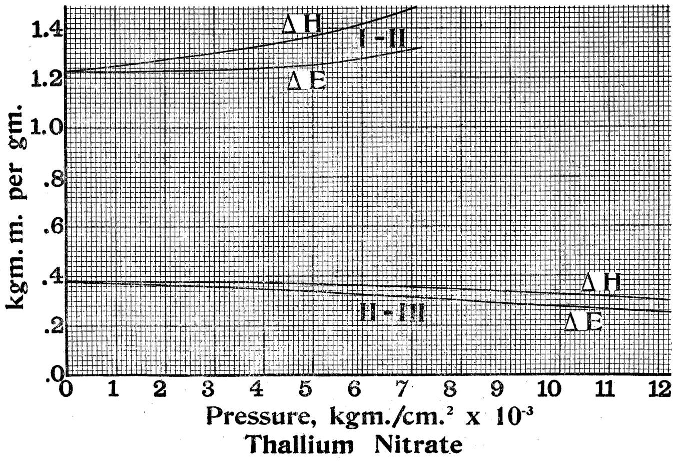

FIGURE 9. Thallium Nitrate. The computed heats of transition and the changes of internal energy.

the highest Δv points. There are enough high points for each transition to determine a pretty good line, and considering that practically all sources of error conspire to give a value of Δv too low, there is considerable probability that the values adopted are near the truth.

TABLE V.

Thallium Nitrate.

Pressure	Temperature	ΔV cm³./gm.	$\frac{d\tau}{dp}$	Latent Heat kgm.m./gm.	Change of Energy kgm.m./gm.
			I-II		
1	144°.6	.00244	.00830	1.22	1.22
1000	152 .9	242	825	1.25	1.23
2000	161 .1	241	815	1.28	1.23
3000	169 .2	239	810	1.305	1.23
4000	177 .3	237	800	1.335	1.24
5000	185 .3	235	790	1.37	1.25
6000	193 .1	234	772	1.41	1.27
7000	200 .7	232	745	1.48	1.31
			II-III		
1	75°.0	.00073	.00668	.38	.38
1000	81 .6	70	655	.38	.37
2000	88 .1	675	643	.38	.365
3000	94 .5	65	632	.38	.357
4000	100 .8	625	624	.375	.350
5000	107 .0	60	616	.37	.34
6000	113 .1	57	611	.36	.325
7000	119 .2	55	606	.355	.315
8000	125 .3	52	603	.345	.30
9000	131 .3	495	600	.335	.29
10000	137 .3	47	596	.325	.275
11000	143 .2	445	592	.313	.265
12000	149 .1	42	587	.302	.25

The latent heat and the change of energy, calculated with the values found above from the curves of t and Δv against pressure are shown in Figure 9. The three modifications behave differently with respect to each other; ΔH and ΔE rising with increasing pressure on the I–II line, and falling on the II–III line. The numerical results are collected in Table V.

There are not many values for comparison. For the transition temperature I–II van Eyk [8] found 142.5°, Gossner [7] 151°, and Wallerant [6] 125°. For the transition temperature II–III Gossner gives 80° and Wallerant 80°. Van Eyk entirely overlooked this transition in his first paper; in a later paper [9] he corrected his earlier results and gives 72.8° by a dilatometric, and 79°–80° by an optical method. The values which I found above for the transition points were 144.6° and 75°. Although these were obtained by extrapolation, the range was small and the presumption is that they are at least as accurate as the other values. My values are means between limits reached by the reaction when running in opposite directions, both phases being present, whereas certainly Gossner and Wallerant did not shut their equilibrium point within values from the two sides, and sometimes give as the transition temperature merely the temperature of appearance of the new phase on heating. There seem to be no previous measurements of the thermal effects of the transition, and the only measurement of change of volume is by van Eyk [9] who found 0.0004 ± cm.^{3}/gm. for the transition II–III.

The difference of compressibility of the phases may be found in the usual way from the difference of the slope of the isothermals above and below the transition. For this purpose only those runs were used which gave good values for Δv. There are nine such good points for the change I–II. Of these, seven show no difference of compressibility and two show a slightly greater compressibility for II. The inference seems justified that within the limits of error the compressibility of I and II are the same. There are six good points for II–III, and all of these indicate that III is the more compressible. Furthermore, these six points are all self consistent and show a decreasing difference of compressibility with rising pressure and temperature. At 75°, the compressibility of III, measured in cm.^{3} per gm. per kgm. per sq. cm., is 0.0_65 greater than that of II, at 105° it is 0.0_63 greater, and at 140°, 0.0_615 greater. It is remarkable that the two phases with the smaller difference of volume should have the greater difference of compressibility. Combining the difference of compressibility with the change of volume along the transition line, the difference of expansion may be computed in the regular way. III turns out to be more expansible; the average difference over a range of 10000 kgm. is 0.00005 cm.^{3} per gm. per °C.

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[8] C. van Eyk, ZS. phys. Chem. **30**, 430–459 (1899).

[9] C. van Eyk, ZS. phys. Chem. **51**, 721–731 (1905).

Most careful search was made for other modifications to 12500 kgm. at 20°, 100°, 150°, and 200°, but no transitions except those found above were detected.

POTASSIUM NITRATE.— This substance was Kahlbaum's purest, used without further purification. It was fused into an open steel shell, thus effectually driving away the moisture, and then the sides of the shell were pierced with fine holes to ensure equality of pressure in all parts. Pressure was transmitted directly by kerosene. Two samples were used. With the first, 39 gm. in amount, all the high pressure points were determined, 21 in number. The second sample, weighing 32 gm., gave several points at low pressures.

Considerable trouble was found in getting the Δv points, and several repetitions were necessary. The discrepancies were always in the direction of too low values. The reason is probably to be found in a combination of the considerable lag which the transition shows, with the effect of fissures, which formed in great numbers on solidification from the melt. The effect of lag is that it is necessary to push the pressure considerably beyond the transition line to ensure the reaction starting, and the effect of fissures may be to prevent the reaction from running completely throughout the entire mass after it has once started in some parts. To be sure that the transition is complete, the pressure must be pushed far enough beyond the transition line to ensure kernels of the new modification appearing in all the parts. The point at 0°, for example, had to be repeated for this reason. To ensure completion of the reaction, when the point was repeated, pressure was maintained 1000 kgm. beyond the equilibrium line at room temperature for three hours, and only then was the temperature lowered to 0°. The first value of Δv, before this procedure was adopted was 25% too low. The sluggishness of the reaction sometimes necessitated special procedure. Thus the lower point on the II–III curve was determined by maintaining temperature for some time at 90° to ensure completion of the reaction from II to III, and then lowering temperature at such a pressure as to land in the corner between the II–III and the III–IV lines. The lag varies considerably with the temperature on the several curves. Thus on the upper end of the II–III curve, III could be considerably subcooled with respect to II, but II could be very little superheated with respect to III.

The sluggishness of the reaction made it impossible to obtain good values for the change of volume between I and III or between II and III at low pressures. Three sets of measurements were made around the triple point I–II–III. The first gave the change of volume I–II by the method of changing temperature at constant pressure. The temperature could be raised so far beyond the transition line that the reaction from II to I was surely complete, and of course it was not difficult to be sure of starting with pure II at low temperature. But this method does not give the temperature of the transition point, and this transition temperature was especially needed in fixing the position of the triple point. To fix this point, pressure and temperature values were obtained at low pressures on the I–III and the II–III lines, by the method of varying pressure at constant temperature. It was possible to shut the pressure within narrow limits, 20 to 30 kgm., but the domain of subcooling was so wide that the reaction was not completed even on reducing pressure to nearly atmospheric. The directly found values of ΔV at these points were 10 to 15% too low. These points were, therefore, discarded. The ΔV curves for I–III and II–III at low pressures were determined by extrapolation from the high pressure values together with the condition that the changes of volume should check with that for I–II at the triple point.

In spite of the comparatively large amount of lag, the width of the band of indifference was not abnormal. No absolute value can be attached to these figures, because of the disturbing effect of fissures. The limits were notably wider on repeating a point, probably because of the fissures formed by the intervening transitions, and were very much less in the low than in the high pressure apparatus. The figures pretend only to give roughly a comparative estimate. The band was widest for the II–IV curve, about 250 kgm.; on the II–III curve it varied from 200 kgm. at the lowest to 100 kgm. at the highest temperature; on the I–III curve the variation with rising temperature was from 100 to 30 kgm., and on the III–IV curve from 140 to 0 kgm. with rising pressure. On all the curves, the band becomes narrower with rising temperature. The reaction, as usual, ran more rapidly at the high temperatures, and at least on the II–III and III–IV curves the transition ran more rapidly in the direction of falling pressure.

The experimental values of pressure and temperature are shown in Figure 10, the experimental values of ΔV in Figure 11, the computed values of ΔH and ΔE in Figure 12, and the numerical results in Table VI. All of the pressure-temperature determinations are shown on the curves, but four of the ΔV points have been discarded for reasons already given.

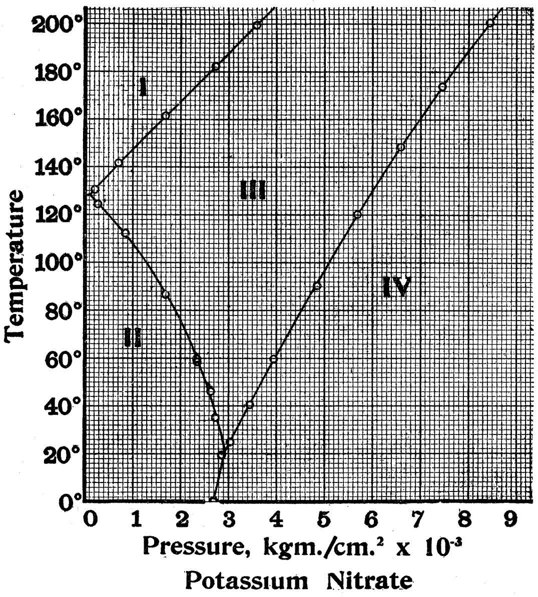

Figure 10. Potassium Nitrate. The observed equilibrium pressures and temperatures.

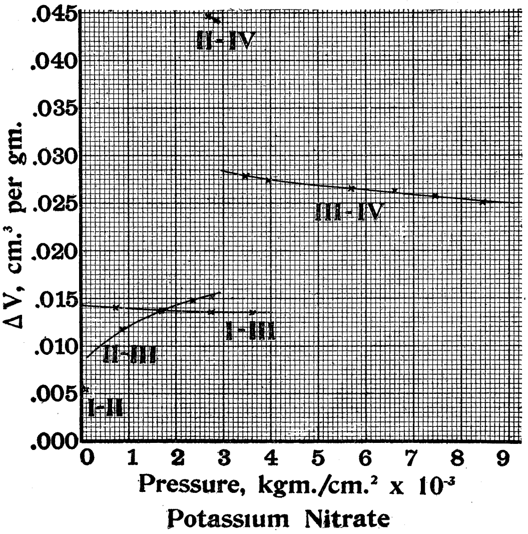

Figure 11. Potassium Nitrate. The observed changes of volume.

The interesting features of the diagram, apart from the two new modifications, are the pronounced curvature of the II–III line, and the great proximity of the I–II–III triple point to atmospheric pressure. It suggests itself that it might be possible under the proper conditions to realize III at atmospheric pressure as an unstable form, and as a matter of fact Wallerant has found an unstable form on cooling I below the triple point to about 114°. This unstable form is uniaxial, but Wallerant was not able to further characterize its crystallographical system.

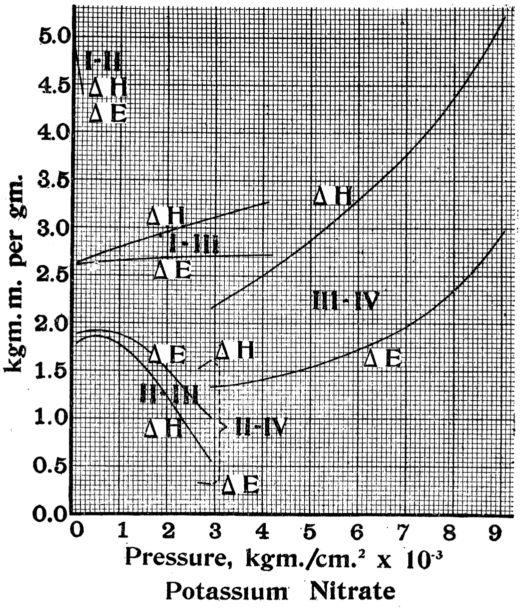

FIGURE 12. Potassium Nitrate. The computed heats of transition and the changes of internal energy.

There are a large number of determinations at atmospheric pressure. For the transition temperature Bellati and Romanese[10] give the limits 128.7° and 121.7° on heating and cooling, Bellati and Lussana[11] give 127.76°, Schwarz[2] gives the limits 121.5° to 129.5° by a thermal method and 129.5° by an optical method, van Eyk [8] gives the limits 125° to 127.8° on heating and cooling, Hissink [3] gives 127.9°, and Wallerant [6] gives 126°. The value found above by extrapolation was 125.8°. This value is probably as near the truth as any of the

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[10] M. Bellati and R. Romanese, R. Ist. Ven. **3**, 653–669 (1884–85).

[11] M. Bellati and S. Lussana, R. Ist. Ven. **2**, 995–1023 (1890–91).

TABLE VI.

Potassium Nitrate (KNO_3).

Pressure	Temperature	ΔV cm³./gm.	$\frac{d\tau}{dp}$	Latent Heat kgm.m./gm.	Change of Energy kgm.m./gm.
			I–III		
1	125°.8	0.01424	.02177	2.609	2.609
1000	147 .1	1394	2091	2.800	2.661
2000	167 .7	1370	2038	2.964	2.690
3000	187 .9	1360	2012	3.115	2.707
4000	207 .9	1354	1995	3.264	2.722
			I–II		
1	127 .7	.0060	.00486	4.95	4.95
			II–III		
510	120 .0	.01050	−.0221	1.867	1.921
1300	100 .0	1286	290	1.654	1.821
1900	80 .0	1410	383	1.303	1.571
2350	60 .0	1480	509	.968	1.316
2690	40 .0	1528	667	.717	1.128
2955	20 .0	1560	841	.544	1.005
			II–IV		
2665	0°.0	.04474	.08032	1.522	.330
2790	10 .0	4440	"	1.565	.326
2920	20 .0	4410	"	1.609	.322

Table VI, Continued.

Pressure	Temperature	ΔV cm^3./gm.	$\frac{d\tau}{dp}$	Latent Heat kgm m./gm.	Change of Energy kgm.m./gm.
III-IV					
3000	23°.9	.02830	.03844	2.187	1.338
4000	61 .4	.02740	.03655	2.508	1.412
5000	96 .8	2680	3438	2.883	1.543
6000	130 .0	2636	3210	3.311	1.729
7000	160 .9	2582	2964	3.780	1.956
8000	189 .2	2540	2680	4.381	2.349
9000	214 .5	2500	2350	5.186	2.936
Triple Point, II-III-IV					
2930	21 .3	II-III .01560	−.0830	.553	1.010
		III-IV .02840	.03860	2.166	1.334
		II-IV .04400	.08032	1.613	.324
Triple Point, I-II-III					
115	128°.3	I-III .01420	.02166	2.631	2.615
		II-III .00886	.0200	1.778	1.788
		I-II .00534	.00486	4.409	4.403

others, because the extrapolation from the triple point is a very short one and does not admit of much question, and the transitions above the triple point, on which the extrapolation is based, do not show the lag effects so prominently as at atmospheric pressure. There seem to be no values of ΔV at atmospheric pressure for comparison. Bellati and Romanese[10] give for the latent heat of the transition 11.89 cal. against 11.6 cal. found above. The agreement is closer than usual. There seem to be no previous measurements of the effect of pressure on the transition.

Several direct determinations of the difference of compressibility were made, which were not, however, very accurate. At the triple point I–II–III, there are no data for the computation, and at the triple point II–III–IV the values are not accurate enough. This much may, however, be stated with some confidence. III is more compressible than I; the difference is of the order of 0.0_51, and probably the difference decreases with increasing pressure: III is also more expansible than I, and the difference is of the order of 0.0_46. The specific heat of I is less than that of III, the difference being about 1 kgm. cm. per gm. II is probably less compressible than III, and it is probable that the difference of expansion between II and III changes sign along the transition curve; at the higher temperature II is less expansible, and at the lower temperatures more expansible. III is more compressible than IV and the difference is of the order of 0.0_51. There is also a direct experimental determination of the difference of specific heats of I and II by Bellati and Romanese,[10] at 0.014 cal., but the authors themselves say that the difference of specific heat cannot be expected to be accurate.

Search was made for other modifications to 12000 kgm. at 20° and 200°, but without success.

Ammonium Nitrate. The material used was Kahlbaum's purest, "zur Analyse," obtained from Eimer and Amend. Two series of runs were made, separated by an interval of a year. For each of these series of runs the material was hammered dry into a perforated steel shell, and the pressure transmitted directly to it by kerosene. For the second run, the salt was subjected to a preliminary drying in vacuum at 100°. No difference in behavior between the two runs to be attributed to this cause was to be detected. The second series, repeating the first, was made necessary by the fact that the measurements of Δv given by the first series were irregular. The reason for this is that ammonium nitrate is a substance for which it is particularly difficult to force the reaction from one phase to another to run to completion. It is very curious that a reaction which will start to run with only a little subcooling or superheating will run to completion only with a much greater subcooling or superheating. I have found this same behavior several times with other substances. It has also been observed for ammonium nitrate by Behn; [12] he found, for example, that for the transition IV–V it was necessary to lower the temperature fully 30° beyond the transition temperature before he could be sure that the reaction was complete, and on raising the temperature he found the same lag also. The phenomenon is more unusual with rising temperature. Upon the repetition of the experiment, error from this effect was avoided only by very careful work, profiting by the experience of the first run. It is necessary to run the pressure several thousand kilograms beyond the equilibrium point in order to be sure of the completion of the reaction. The completion of the reaction is also greatly facilitated by running the pressure back and forth several times over the transition before beginning the measurements. In the neighborhood of the triple point II–III–IV, where it is not possible to secure completion of the reaction by running the pressure over a considerable range, because the pressure of equilibrium is too near atmospheric pressure, the same end was attained by raising or lowering the temperature, as occasion might require, and then bringing it back to the temperature of the measurement. I had

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[12] U. Behn, Proc. Roy. Soc. **80**, 444–457 (1907–08).

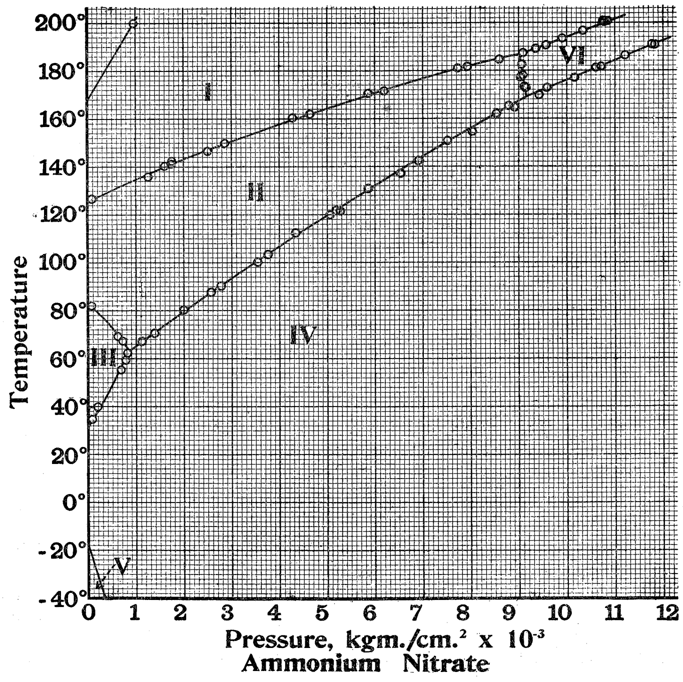

FIGURE 13. Ammonium Nitrate. The observed equilibrium pressures and temperatures.

not thought of this trick of procedure at the time the measurements in the neighborhood at the triple points I–II–IV–VI were made, and some error is introduced into the actual data which it would have been possible to avoid if the measurements had been repeated. However, the values of the changes of volume at these points seem to be indicated with sufficient certainty. At low pressures, where the method is that of varying temperature at constant pressure, lag is not so troublesome, and repetition was not necessary. The low pressure point on the curve I–II was not repeated; the repeated points at low pressure for the transitions II–III and III–IV were in substantial agreement with the first determinations.

The experimental values for the equilibrium pressures and temperatures and the transition curves are shown in Figure 13, the experimental points and the curves for the change of volume in Figure 14, the computed values for the latent heats and the change of internal energy in Figure 15, and the numerical values are collected in Table VII. In the equilibrium diagram the points of both runs, in 1913 and 1914, have been included, but in the change of volume diagram, only the points of 1914 have been given. The irregularities of the early points for Δv were so great that it was almost hopeless to attempt to obtain any information from them.

Several features of these diagrams require special comment. The phenomenal steepness of the melting line is to be noticed. The point on the melting line at 200° was determined experimentally, but for the point at atmospheric pressure I have adopted the value of Lehmann.[13] An attempt to determine this point directly did not give satisfactory results, because of decomposition. This decomposition could be plainly detected at 200°, producing a rounding of the corners of the curves, so that the value for the change of volume cannot be counted on with much certainty. At the melting point at atmospheric pressure the decomposition was so much greater that it did not seem worth while to attempt to calculate a probable value for the change of volume at atmospheric pressure. The decomposition at atmospheric pressure has been found by other observers also; Behn [12] states that it is noticeable at temperatures as low as 100°. It would seem, however, that this decomposition is an effect chiefly found only when the liquid phase is present, or at least that it is effectively prevented by the higher pressures, because no trace of it was ever found on any of the transition curves between solids, even as high as 200°.

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[13] O. Lehman, ZS. Kryst. **1**, 97–131, (1877).

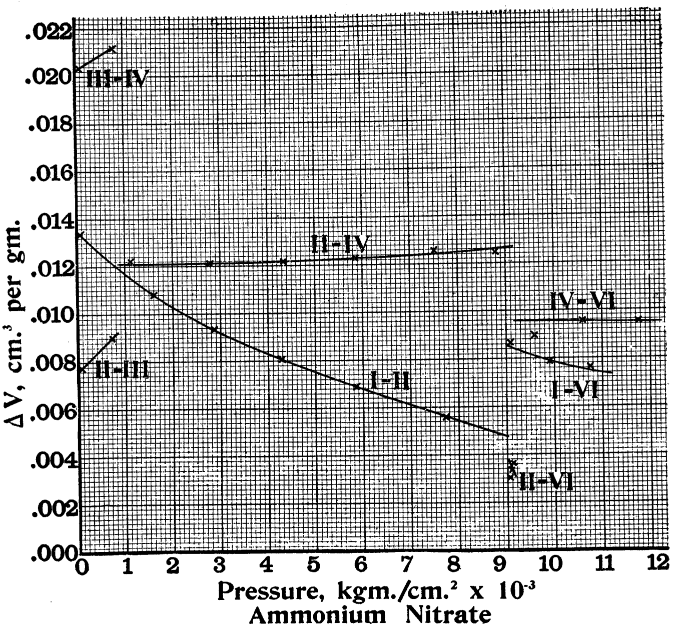

FIGURE 14. Ammonium Nitrate. The observed changes of volume.

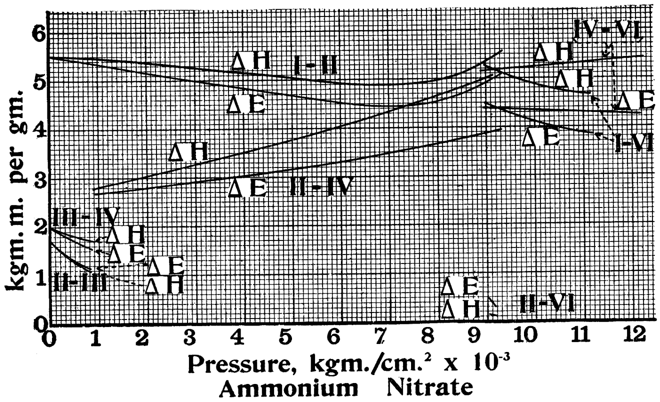

FIGURE 15. Ammonium Nitrate. The computed heats of transition and the changes of internal energy.

The curve drawn for the change of volume between II and VI perhaps requires special comment. This has been drawn as falling with rising pressure, although the points actually obtained would indicate the reverse state of affairs. But the relations at the two triple points terminating this curve demand that the curve shall be as

TABLE VII.

Ammonium Nitrate.

Pressure	Temperature	ΔV cm³./gm.	$\frac{d\tau}{dp}$	Latent Heat kgm.m./gm.	Change of Energy kgm.m./gm.
			Liquid - I		
1	168°		.034	6.9	6.6
1000	202°	.051±			
			I–II		
1	125°.5	.01351	.00974	5.53	5.53
1000	134 .7	.01171	875	5.46	5.35
2000	143 .0	.01028	797	5.37	5.16
3000	150 .7	.00916	738	5.26	4.98
4000	157 .8	828	691	5.16	4.83
5000	164 .5	751	651	5.05	4.67
6000	170 .8	679	613	4.92	4.51
7000	176 .7	610	562	4.88	4.45
8000	182 .0	542	496	4.97	4.54
9000	186 .6	476	409	5.35	4.92
			II–III		
1	82°.7	−.00758	−.0159	1.70	1.70
200	79 .2	797	190	1.48	1.50
400	75 .1	836	221	1.32	1.35
600	70 .4	874	253	1.19	1.24
800	65 .0	913	284	1.09	1.16

Table VII, Continued.

Pressure	Temperature	ΔV cm³./gm.	$\frac{d\tau}{dp}$	Latent Heat kgm.m./gm.	Change of Energy kgm.m./gm.
II–IV					
1000	65°.3	.01210	.0146	2.81	2.69
2000	79 .6	1211	141	3.04	2.80
3000	93 .4	1212	136	3.27	2.91
4000	106 .8	1215	131	3.52	3.03
5000	119 .7	1220	127	3.77	3.16
6000	132 .2	1228	123	4.05	3.31
7000	144 .3	1238	119	4.34	3.48
8000	156 .0	1250	115	4.66	3.66
9000	167 .4	1265	111	5.01	3.87
III–IV					
1	32°.0	.02026	.0311	1.99	1.99
200	38 .5	2051	336	1.91	1.86
400	45 .4	2077	360	1.84	1.76
600	52 .9	2102	385	1.78	1.65
800	60 .8	2128	410	1.73	1.56
IV–V					
1	−18°.0	−.017±	−.063	0.69	0.69
I–VI					
9000	186°.6	.00858	.00750	5.26	4.49
10000	194 .1	785		4.89	4.11
11000	201 .6	740		4.68	3.87
II–VI					
9154	170°.0	.00312	−.125	.111	.296
9034	185 .0	373		.137	.474

Table VII, Continued.

Pressure	Temperature	ΔV cm³./gm.	$\frac{d\tau}{dp}$	Latent Heat kgm.m/.gm.	Change of Energy kgm.m./gm.
VI–IV					
9000	167°.9	.00959	.00820	5.16	4.29
10000	176 .1	955		5.23	4.28
11000	184 .3	952		5.31	4.26
12000	192 .5	950		5.40	4.25
TRIPLE POINT, II–III–IV					
860	63°.3	III–IV .02135	.0417	1.72	1.54
		II–III .00925	.0294	1.06	1.14
		II–IV .01210	.0146	2.78	2.68
TRIPLE POINT, I–II–VI.					
9020	186°.7	I–II .00475	.00406	5.38	4.95
		I–VI .00855	.00750	5.24	4.47
		II–VI .00380	−.125	.14	−.48
TRIPLE POINT, II–IV–VI					
9160	169°.2	II–IV .01267	.0111	5.06	3.91
		II–VI .00309	−.125	.11	.38
		IV–VI .00958	.00820	5.17	4.29

drawn, and considerations of the effect of incompleteness of the reaction also indicate that the curve as drawn corresponds to the actual facts. Thus, the change of volume between VI and IV found at 173° is too small to lie on the curve through the points at higher pressures by precisely the same amount that the change of volume II–VI at the same temperature is too high to fall in with the values demanded by the necessary conditions at the triple points. The explanation is obviously that the reaction from IV to VI was not complete because it was not possible to lower the pressure far enough, and that the reaction was completed when the pressure was carried across the line VI–II, the rest of the change from IV to VI appearing as part of the change from VI to II.

The data for the transition IV–V shown in the table and the diagram were taken directly from the paper of Behn.[12] Because of the great stickiness of the reaction it would have been necessary to set up special apparatus for reaching temperatures at least as low as —50° if accurate measurements of this transition were to be expected, and it did not seem worth while to do this. The slope of the transition line IV–V was not given by Behn, but has been computed by me from his data. Behn states that he was not able to get values for the change of volume which were self consistent to better than 20%, so the value given for the slope may be in error by as much as this.

The results for ammonium nitrate are different in one or two interesting particulars from those found for most other solid transitions. The change of volume II–IV increases with rising pressure instead of decreasing, as it has for every other substance previously investigated. The change of volume between III and IV also shows the same effect. This is probably to be attributed to unusual properties of IV, as will be brought out in a later discussion of the relations of the compressibilities, thermal expansions, and specific heats. It is also very unusual, although this is not the only example, that the III–IV line is concave upwards. That this is true is indicated by several independent lines of evidence.

A good deal of work has been done on this substance by other experimenters at atmospheric pressure, and there are at least two pieces of work on the effects of pressure. The existence of four modifications at atmospheric pressure has been known for some time, but it is not so commonly mentioned that there is a fifth modification. This seems to have been first discovered by Lehmann, was then studied by Wallerant,[6] and more lately by Behn[12]; its existence seems absolutely beyond question. The problems offered by this low temperature form are of great interest. Wallerant was able to find that its crystalline system was the same as that of II, and he suggested that it was in fact the same modification. This appearance of the same phase in two isolated parts of the phase diagram is unique, if it should be proved, but seems to be not contrary to any of the thermodynamic necessities. Behn has subjected the question to a very careful experimental examination, measuring the various thermal and crystallographical properties of II and V to see whether it is possible to state an indentity. His data did not allow of a definite answer to the question, but seem to suggest that II and V are not the same phase. I did not make any measurements on this transition for the reasons already stated, but did investigate one questionable point. One might expect, since the transition IV–V is of the ice type, that at higher pressures another phase would exist, so that the falling transition curve between IV and V would be replaced by a rising curve between IV and the new modification. I did not find any such new modification out to 12500 kgm. at room temperature.

The following transition temperatures are found in the literature. For I–II Lehmann [13] gives 127°, Bellati and Romanese [14] give the limits 124° to 125°, Lussana [15] found the limits 124.9° and 125.6°, and Schwarz [2] has found the value 125.6° by one method, and the limits 123.5° to 125.5° by another. In the table I have given 125.5° as agreeing best with my own data and the best results of other observers. For the transition II–III Lehmann [13] gives 87°, Behn [12] gives 83°, Bellati and Romanese [14] give the limits 82.5° to 86°, Schwarz [2] gives the limits 82.5° to 86.5° by one method, 82.8° to 82.7° by another, and 83° by a third, Wallerant [6] gives 82°, Tammann [16] gives by extrapolation from his measurements at higher pressures the value 84.6°, and Lussana [15] finds that the transition takes place at 85.85° on heating, but does not give the value on cooling. I have adopted the value 82.7° as agreeing best with my own data and those of others. For the transition III–IV Lehmann [13] gives 36°, Bellati and Romanese [14] give the limits 31° to 35°, Schwarz [2] gives the limits 31° to 35° by one method, 32.4° (best) by another, and 35° by a third, Wallerant [6] gives 32°, Behn [12] 32°, Tammann [16] finds by extrapolation from his high pressure measurements 31.8°, and Lussana [15] finds the limits 35.45° and 30.55° on heating and cooling. I have adopted the value 32.0°. There are only three measurements of the transition IV–V. Lehmann (in a personal letter quoted by Behn)[12] gives −16°, Wallerant gives the limits −14° to −16°, and Behn finds −18°. I have adopted this last value as more probably exact. For the melting point I have adopted the value of Lehmann, 168°, which is somewhat higher than the value given by Behn, 166°, as the average of several other determinations. As already stated, I made no attempt to measure this point myself.

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[14] M. Bellati and R. Romanese, R. Ist. Ven. **4**, 1395–1420 (1885–86).

[15] S. Lussana, Nuov. Cim. (4), **1**, 97–108 (1895).

[16] G. Tammann, Kristallisieren und Schmelzen, Barth, Leipzig (1903), p. 299.

The change of volume at atmospheric pressure has been measured by Bellati and Romanese[14] for the transitions IV–III and II–III. For III–IV they give 0.01964 cm.^{3} per gm., but from a recomputation of their data I should prefer the value 0.01955, although their data show enough irregularity to admit a value as low as 0.01915. Behn[12] gives for this transition 0.022 (he pretends to give only two significant figures), and I find by extrapolation from 77 kgm. (the extrapolation correction is less than one percent) the value 0.02026. For the transition II–III Bellati and Romanese give −0.00854 cm.^{3} per gm., Behn gives 0.0081, and I find by extrapolation from 77 kgm. a somewhat lower value, 0.00758, the total extrapolation correction in this case being about 3%. The change of volume I–II was not measured by Bellati and Romanese. Behn gives 0.0132, and I find by an extrapolation from 77 kgm. 0.01351. Lussana[15] did not measure the change of volume, but calculates from his other data for the pressure effect the value 0.01465, assuming Bellati and Romanese's value for the latent heat. The change of volume IV–V seems to have been measured only by Behn, who found that it lies between the values 0.0155 and 0.0185, but was not able to get it more accurately because of the lag already mentioned.

The latent heats of transition have been measured only by Bellati and Romanese,[14] who give for III–IV 5.02 gm. cal. per gm., for III–II 5.33 cal., and for II–I 11.86 cal. I find by calculation from Clapeyron's equation the values 4.66, 4.00, and 13.0 cal. respectively.

The only measurements of the effect of pressure are by Lussana[15] and Tammann.[16] Tammann's measurements extended to 2800 kgm. and include points on the II–III, III–IV, and II–IV curves, but he made no measurements on the phase I. Lussana's pressure range was only 250 kgm.; he measured the three transitions III–IV, III–II, and II–I. Tammann states that there is no possibility of agreement between his values, those of Lussana, and those computed from the thermodynamic data of Bellati and Romanese. The discrepancy stated by Tammann as existing between Lussana's data and those to be computed from the data of Bellati and Romanese appears to be due to an error of Tammann's in converting Lussana's data, which are given in atmospheres, to kilograms. Lussana himself states that the agreement of his experimental values with the computed values is almost perfect, and I have verified this, at least within one of two percent. The apparent discrepancy between Tammann's and Lussana's observations may furthermore be at least partly explained by the difference in the pressure range, because of the fact that the slope of the transition lines III–IV and III–II changes markedly with pressure. The slope of the line II–III decreases algebraically, the normal direction of variation, but the slope of the line III–IV increases with rising pressure, a somewhat unusual effect. These two equilibrium lines are so short that it would be a matter of considerable experimental difficulty to accurately measure the variation of slope with pressure. That there is a variation with pressure was first suggested to me by an examination of my own equilibrium points. Furthermore, on making the computations, it appeared that such a variation was imperatively demanded by the conditions at the triple point. With the help of the known relations at the triple point it was possible to get a fairly good idea of what the actual variation of slope must be. The values given in the Table were computed so as to satisfy the conditions at the triple point, and with no other conditions in mind. In fact, I did not know of the discrepancy between the values of Lussana and Tammann until after I had made the computations. All of the discrepancy between these observers cannot be explained in this way, however. Lussana gives for the slope of the transition III–IV over a range of 250 kgm. 0.0287, Tammann gives over the range up to the triple point, that is up to 860 kgm., the average slope 0.0346. I find for the average slope up to the triple point 0.0364, and for the average over the first 250 kgm. 0.0318. The variation of slope with pressure is fairly large and will explain a large part of the discrepancy between Tammann and Lussana, although it will evidently not account for all of it. The agreement of Tammann's and my results is better than that of Tammann and Lussana. It must be said that Tammann did detect the curvature of the transition lines, and states that the II–III curve is concave downwards and the III–IV concave upwards, but he makes no allowance for this fact in comparing his results with those of Lussana. In spite of the surprisingly good agreement found by Lussana between his results and those computed from the thermal data of Bellati and Romanese, this agreement must be recognized as accidental, and not necessarily indicating the correctness of the data of either Bellati and Romanese or of Lussana. Lussana's method was not one adapted to give accurate results. He measured the time rate of heating or cooling and took the arrest points as the points of transition. These points differed by 5°, and the mean of the two points was taken as the true temperature of transition. The total effect of pressure over the range of 250 kgm. was little more than the width of the band of indifference of the individual measurements. The insensitiveness of the method is indicated by the fact that he found no variation of slope with pressure, whereas the variation ought to have been easily perceptible even over this low range. Lussana nevertheless, gives the results to three significant figures.

On the III–IV curve the conditions are similar to those on the II–III curve. Lussana gives for the slope over the first 250 kgm. 0.0137 against 0.0135 computed, and Tammann gives for the range up to the triple point the average slope 0.0220. I find for the average slope over the first 250 kgm. 0.0178, and for the average slope up to the triple point 0.0226, in substantial agreement with Tammann. A thoroughgoing comparison of my results with those of Tammann is not possible, because he has not taken any account of the known curvature of the transition line in computing the values at atmospheric pressure. It is evident, however, that both his results and mine would differ in the same direction from the only other data at atmospheric pressure, namely those of Bellati and Romanese, and also from those of Lussana. It seems probable that there may be some considerable experimental error in the data of Bellati and Romanese, and that the curvature of the III–IV curve, although large, can account for only part of the discrepancies.

The coördinates that Tammann finds for the triple point II–III–IV are considerably different from mine. He finds 64.16° and 930 kgm. against my values 63.3° and 860 kgm. For the average slope of the II–IV line between the triple point and 90° Tammann finds 0.01404 and I find 0.01416. The agreement is better than usual.

The pressure effect on the transition I–II has been previously measured only by Lussana. He finds 0.0116 for the average slope over the first 250 kgm. against my value 0.00962.

The measurements of the difference of compressibility of the different phases at high pressures did not give any very regular results. This much may be stated, however; I is more compressible than II, of the order 0.0_68, and is more compressible than VI of the order 0.0_65, and IV is more compressible than II of the order 0.0_68. This last is an unusual feature, because IV is the phase stable at higher pressures and lower temperatures. That the relation of the compressibilities of II and IV is unusual might be also suggested by the fact, already mentioned, that the change of volume becomes greater at the higher pressures. The other differences between I, II, IV, and VI may be obtained by a combination of the values given above. The experimental data were not accurate enough to allow a statement as to the variation of difference of compressibility with pressure on the transition line; the above values are average values. No direct values were obtained on the short lines II–III and III–IV.

I was also able to obtain fairly satisfactory measurements of the difference of thermal expansion of III, IV, and II at 77 kgm. II is more expansible than III, the difference being 0.000038 cm.^{3} per gm., and IV is more expansible than III by 0.000115. Here again, the behavior of IV is anomalous, being more expansible than a phase stable at a higher temperature. The thermal expansions at atmospheric pressure have been measured by Bellati and Romanese [14] and by Behn.[12] One may deduce from the data of Bellati and Romanese, although the authors themselves do not give the computation, that the expansion of IV is 0.000222 cm.^{3} per gm., that of III 0.000134, and that of II 0.0001165. The differences between these values do not agree at all with the values which I have found, in fact they would make II less instead of more expansible than III. The values of Behn I have computed from a diagram which he gives; he himself does not give the computations. From his data I would make the expansion of II 0.00041 cm.^{3} per gm., that of III 0.00036, that of IV 0.00048, and that of V 0.00037. The differences between II and III and between III and IV will be seen to agree remarkably well with the values which I found above. There seems to be no doubt that IV is more expansible than III, and that II is more expansible than III.

The specific heats at atmospheric pressure has been measured by Bellati and Romanese.[14] They find for IV 0.407 cal. per gm., for III 0.355 cal., and II 0.426. Here again IV is abnormal, its specific heat being greater instead of less than that of the high temperature phase.

If now we compute in the regular way the differences of compressibility and specific heats at atmospheric pressure, using the values which may be deduced from Table VII for the variation of the change of volume and the latent heat with pressure along the transition curve, and assuming my direct experimental values for the differences of thermal expansion, we shall find that II is more compressible than

III by 0.0_513, and III is less compressible than IV by 0.0_538. This verifies the abnormally high compressibility of IV again. Computations made in the same way give for the difference of specific heats between II and III 0.16 cal. against Bellati and Romanese's [14] direct value 0.071, and for the difference III–IV 0.048 cal. against their value 0.052. This verifies the abnormal sequence of the specific heats II–III–IV, and the numerical values agree as well as one could expect when one considers that the method of computation employed above throws by far the larger part of the error into the specific heats. This has already been fully explained in a preceding paper.

The question of the time rate of the various transitions and the lag phenomena will be dealt with in greater detail in another paper. It will not be out of place to mention here, however, that many measurements were made of the time rate, and at all points it was found that the rate is greater with decreasing pressure, as has also been found for most other substances.

Nitrates with no New Forms.

The following nitrates were examined without result for other forms between 1 and 12000 kg. at 20° and 200°; $NaNO_3$, $LiNO_3+Aq$, $Hg_2(NO_3)_2$, $Hg(NO_3)_2$, $Pb(NO_3)_2$, $Al(NO_3)_3$.

Sodium, although chemically similar in many respects to potassium and the other alkali metals whose nitrates are polymorphic, is in its crystalline properties known to be so much dissimilar that its salts do not form isomorphic mixtures. From this point of view, it is therefore not surprising that no new forms were found. $NaNO_3$ (which is trigonal) does, however, crystallize isomorphously with the high temperature form (trigonal) of $AgNO_3$, and will crystallize in small percentages isomorphously with the low temperature form. We suspect, therefore, that $NaNO_3$ has a second modification, stable at low temperatures at atmospheric pressure. It would be interesting to search for this. Hissink [3] has found no new form between 270° and $-50°$. The transition, if it exists, is by analogy with $AgNO_3$ of the ice type, the transition curve falling with rising pressure. It is natural that no new form was found at high pressures at room temperature.

$LiNO_3$ is probably not isomorphous with $AgNO_3$ or $NaNO_3$, although Retgers says that it is with the latter. There is no necessity for expecting other forms. Arzruni, however, on authority which goes back to 1857,[17] says that $LiNO_3$ is trimorphic. Other authorities, Groth included, do not mention this, however, and the supposed polymorphism is doubtless to be explained as due to the transition points of the hydrates, because $LiNO_3$ crystallizes with H_2O. I made especially careful search for other forms, isothermally at 20° and 200° to 12000 kg., and at constant volume between 100° and 160° at approximately 3000 kg. and between 30° and 160° at 8000 kg.

$Hg_2(NO_3)_2+H_2O$ does not crystallize isomorphously with the other univalent nitrates. The anhydrous salt showed no new form at 20° or 90°. At the higher temperature there was probably some decomposition; temperature was not raised higher for fear of further decomposition. The salt crystallizing with one molecule of water probably has a transition point at 20° at 8000 kg.; no other temperature was tried. The substance is a difficult one to investigate, because beside containing water of crystallization it is hygroscopic. It is difficult to remove the absorbed moisture without dehydration. The material deserves further investigation, however.

$Hg(NO_3)_2$ was the first of the nitrates tried which was not univalent. I know of no cases of polymorphism among this class; there is no particular reason to expect other forms at high pressures. $Hg(NO_3)_2$ showed nothing new at 20° to 12000; on heating to 180° at 1000 kg. it decomposed with almost explosive violence, depositing metallic mercury throughout the apparatus.

$Pb(NO_3)_2$ is stated by Arzruni [18] to exist as a mineral in two forms. I found no new form up to 12000, however, at 20° or 200°.

$Al(NO_3)_3$ was tried at 20°, 100°, and 200° with no effect. After the run it was found to have decomposed into a brownish mass, actively deliquescent. It was somewhat moist before the run.

DISCUSSION.

Most of the facts described in this paper are collected and exhibited qualitatively in Figure 16, which shows the phase diagrams, pressure against temperature, and indicates other data also. The drawings are made with some exaggeration, so that the direction of curvature of each transition line may be readily noticed. The arrows on the lines show the directions in which Δv decreases numerically. An α, β, or C_p placed near a transition line, on one side, shows that the phase on that side of the line has the greater compressibility, thermal expansion, or specific heat. In addition, the Arabic numerals placed in the regions of the several phases show the crystalline systems. The Roman numerals give the designation of the phases used in the early part of this paper. The information about the crystalline systems has been taken directly from Wallerant's Cristallographie, a work which deserves to be better known in this country.

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[17] P. Kremers, Pogg. Ann. **92**, 520 (1854) and **93**, 23 (1854).

[18] A. Arzruni, Physikalische Chemie der Krystalle. Vieweg und Sohn, Braunschweig (1893), p. 42.

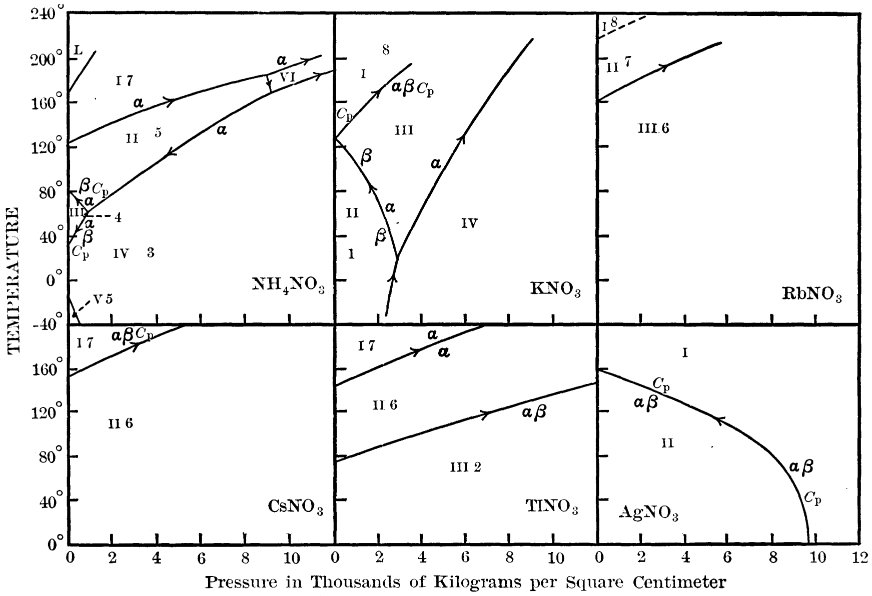

FIGURE 16. Collection in one diagram of the several phase diagrams. The Arabic numerals refer to the crystalline systems as follows:

1, Quasi-trigonal.
2, Orthorhombic, quasi-tetragonal, optically negative.
3, Orthorhombic, quasi-tetragonal, optically negative.
4, Monoclinic, quasi-tetragonal, optically positive.
5, Tetragonal, optically positive.
6, Rhombohedric, quasi-cubic, optically positive.
7, Cubic.
8, Rhombohedric, type of calcite, optically negative.

It is evident in the first place that $AgNO_3$ belongs in a class apart from the other five univalent nitrates. Its phase diagram is entirely different in character, and it is known not to crystallize isomorphously with any of them. $AgNO_3$ may be disregarded in any comparative study, therefore, and in the following only the five alkaline nitrates are considered.

A comparison of the phase diagrams is more significant when we combine with it a discussion of the mixed crystal relations. Wallerant has given in his book a most elaborate account of the mixed crystal situation, and I shall draw my data from him.

One conclusion to be drawn from this discussion will be that similarity of phase diagrams is evidence of the most complete similarity of structure, more complete even than the ability to form continuous series of mixed crystals. Judged by this latter test, the five alkaline nitrates are very similar. Wallerant has proved that every one of the five can form mixed crystals in limited proportions with every one of the atmospheric polymorphic forms of all the other nitrates. The phase diagrams are not the same, however, for all five nitrates; those of Rubidium, Caesium, and Thallium are most similar. Each of these three diagrams contains a transition line between the cubic form (7) and the orthorhombic, pseudo-hexagonal, form (6). The use of the same numerals for these phases in the different diagrams is justified by the fact that within the proper temperature range the phase 7 or 6 of any of the three salts will form a continuous series of mixed crystals with the phase 7 or 6 of any of the others. We may call the line 7–6 the "same" line in the various diagrams. This line preserves various of its characteristics with very little change from substance to substance, as is shown by the summary in Table VIII.

The lines 7–6 correspond so closely that we expect further similarity of the phase diagrams of these three salts. We should expect for

TABLE VIII.

PROPERTIES OF TRANSITION LINE 7–6.

Substance	Average slope	Average Δv cm.³/gm.	%	Curvature	Variation of Δv
$RbNO_3$	.009	.0052	1.5	Normal	Normal
$CsNO_3$	.009	.0035	1.3	"	"
$TlNO_3$	.008	.0024	1.3	"	"

$CsNO_3$ and $TlNO_3$ a line 8–7 like that of $RbNO_3$. Such a line has not been found, however. Failure to find it for $TlNO_3$ is not strange; the transition 8–7 may well have risen above the melting point, which is comparatively low, only 205°. But failure to find it for $CsNO_3$ is not so easy to explain. If the transition point has risen above the melting point, which for $CsNO_3$ is at 414°, the effect of increasing molecular weight on the transitions 8–7 and 7–6 is very different in going from $RbNO_3$ to $CsNO_3$; the latter is depressed from 164° to 154°, while the former would be raised from 219° to over 414°. It seems quite possible that the transition for $CsNO_3$ may have been overlooked, and that a careful search up to 414° would be worth while. The mixed crystal diagrams of $RbNO_3$ with $CsNO_3$ and $TlNO_3$ suggest that both the latter salts would show the modification 8 if it were not for the interference of the liquidus line.

With regard to the transition 6–2 of $TlNO_3$ there is certain indirect evidence that such transitions exist for both $CsNO_3$ and $RbNO_3$, although their existence has not been directly proved. Wallerant states that $CsNO_3$ passes to another modification on cooling in liquid air. The crystalline form of this new modification he found to be rhombohedric, approximately cubic. This is not the same as the crystalline system of $TlNO_3$, 2, which is orthorhombic, but the difficulty of crystallographic observation at very low temperatures does not make it absurd to suppose that the system may have been incorrectly determined. The existence of another modification is of itself significant. With regard to $RbNO_3$, Wallerant's observations on mixed crystals of the system $NH_4NO_3 - RbNO_3$ make it almost certain that at low temperatures $RbNO_3$ has another modification. In the mixed crystal diagram there is a range of concentration, varying with temperature, within which $RbNO_3$ and NH_4NO_3 crystallize together in a form with all the characteristics of $TlNO_3$, 2, a form which has not been found for either pure $RbNO_3$ or NH_4NO_3. An easy extrapolation of the region of the mixed crystals indicates at low temperatures the existence of the phase as pure $RbNO_3$. I am not aware that Wallerant made the same examination of $RbNO_3$ down to liquid air that he did of $CsNO_3$. If it should turn out that $RbNO_3$ and $CsNO_3$ have the phase 2, the transition point to 6 would be quite differently situated for these two salts than it is for $TlNO_3$. This need not be surprising; the work of Tutton on the sulfates, for example, has shown that although the Thallium salts are closely related to those of the alkaline metals proper, yet a detailed analysis shows abrupt discontinuites in the numerical magnitudes.

The diagram of KNO_3 next demands attention. The phase I or 8 is the same as the phase 8 of $RbNO_3$. It is most tempting to call the new high pressure phase III the same as 7 and IV the same as 6, for this would mean that at high pressures, by a simple displacement of the origin of pressure, the diagram of KNO_3 takes its place with those of higher molecular weight, $RbNO_3$, $CsNO_3$, $TlNO_3$. Furthermore, a shift of the pressure origin in this direction, corresponding to a decrease in molecular weight, seems a not unnatural result of the corresponding decrease of internal pressure. It is unfortunate that a comparison of numerical results is not favorable to this identification. The only data which we can use are for the line III–IV; we are to inquire whether this can correspond to the line 7–6 of $RbNO_3$, $CsNO_3$, and $TlNO_3$. The slope of the line III–IV is 0. 3, while that of 7–6 varies from 0.008 to 0.009 and the change of volume on the line III–IV is 5.5% against 1.6, 1.3, and 1.3% respectively for the other three salts. Another bit of presumptive evidence against the identification of III with 7 is that the unstable form of KNO_3 found below the transition I–II at atmospheric pressure is rhombohedric. It is plausible, but not necessary, to suppose that this unstable form is the same as III. But the form of 7 is cubic. The evidence is not conclusive either way, however, and it would be worth while to make special effort to find the system of KNO_3 III; the triple point I–II–III is at such a low pressure that it would not be out of the question to try for a microscopic examination in a heavy glass capillary.

In the case of NH_4NO_3 the probability is fairly good that the new phase VI stable only at high pressures is the same as 6 of Rb, Cs, and Tl. This is indicated not only by its position with respect to 7 (NH_4NO_3, I) but also by the numerical values. The average slope of 7–VI is 0.0075 and the change of volume 1.4%; both of these are very close to the corresponding values for the Rb, Cs, and Tl salts. The probability is further much increased by the mixed crystal diagrams of NH_4NO_3 with $RbNO_3$ and $CsNO_3$. Mixed crystals of $RbNO_3$ or $CsNO_3$, 6, are stable over a very wide range of concentration, which comes closest to pure NH_4NO_3 at the same temperature as that indicated by an easy extrapolation of the line I–VI for NH_4NO_3 to atmospheric pressure. The same argument cannot be applied to the mixed crystal diagram of NH_4NO_3 with $TlNO_3$ because of the anomolous behavior of NH_4NO_3, II.

To make the correspondence of NH_4NO_3 with the heavier nitrates complete, the phase IV of NH_4NO_3 should be identical with III of $TlNO_3$. But both Groth and Wallerant treat these two phases as not the same, calling the first 3 and the second 2. It is significant, however, that crystallographically, both these phases are remarkably similar; Wallerant describes both as orthorhombic, quasi-tetragonal, optically negative. The chief argument against their identity seems to be that they do not form a continuous mixed crystal series, but such a continuous series would be impossible in any event because of the anomolous behavior of the tetragonal form II. In fact it is the peculiar behavior of the tetragonal form that supplies Wallerant with the argument that the forms II and V of NH_4NO_3 are identical. On the whole, the evidence does not seem to me conclusive that 3 and 2 are not identical; in view of the suggestiveness of the phase diagrams, further crystallographic investigation would be desirable. At any rate it is significant that the phases 3 and 2 are so much alike.

Further identification of the phases of NH_4NO_3 is probably not possible; the phases 4 and 5 are not likely to exist in the other nitrates. These phases, if they are capable of existence at all elsewhere, are probably to be found at considerable negative pressures, which we cannot realize experimentally. On the other hand, it would not be strange if NH_4NO_3 had modifications peculiar to itself. The Radical NH_4 cannot be surrounded by so simple a field of force as a single atom of Potassium, Rubidium, Caesium, or Thallium, and it is not surprising if in virtue of its greater complication larger numbers of stable forms are possible. Tutton has found the same behavior among the sulfates.

SUMMARY.

The phase diagrams between 0° and 200° and from 1 to 12000 kg. have been determined for NH_4NO_3, KNO_3, $RbNO_3$, $CsNO_3$, $TlNO_3$, and $AgNO_3$. One new phase has been found for NH_4NO_3 and two new ones for KNO_3. The usual thermodynamic data, which include change of volume, latent heat of transition, difference of compressibility, thermal expansion, and specific heat, are given.

$AgNO_3$ stands in a class by itself. The nitrates of Rb, Cs, and Tl have closely similar phase diagrams. The more complicated diagrams of KNO_3 and NH_4NO_3 may be brought into relation with these by a proper identification of the new high pressure forms with the atmospheric forms of $RbNO_3$, $CsNO_3$, $TlNO_3$. Additional crystallographical work seems necessary, however, before this identification can be established. It is significant that at high pressures the diagrams of all five nitrates tend to the same simple type; the disturbing complications are found only at low pressures.

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